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HYDRODESULFURIZATION CATALYST FOR HYDROCARBON OILS AND METHOD  
FOR PREPARING THE SAME

[Tankasuiso Yu no Suisokadatsuryu Shokubal oyobi  
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## SPECIFICATION

(54) [Title of the Invention]

Hydrodesulfurization Catalyst for Hydrocarbon Oils and  
Method for Preparing the Same

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[Claims]

[Claim 1] A hydrodesulfurization catalyst for hydrocarbon oils which is characterized in that the catalyst is made by depositing 1 ~ 30 mass% of alumina or silica-alumina, 1 ~ 3 mass% of sulfate radical in terms of the sulfur content and 0.05 ~ 10 mass% of palladium on a carrier consisting of zirconium oxide or hydroxide, the total pore volume is 0.1 mL/g or above and the proportion of pores of 1.4 ~ 2.1 nm in pore diameter therein is 30 ~ 70%.

[Claim 2] A hydrodesulfurization catalyst which is characterized by further depositing 0.05 ~ 10 mass% of one, two or more selected from platinum, rhenium, ruthenium, cobalt and

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<sup>1</sup>Numbers in the margin indicate pagination in the foreign text.

molybdenum on the basis of catalyst in the catalyst according to Claim 1.

[Claim 3] A method of preparation which is a method for preparing the hydrodesulfurization catalyst according to Claim 1 or 2 and comprises treating a zirconium hydroxide carrier with a treating agent for giving a sulfate radical thereto, depositing 1 ~ 3 mass% of sulfate radical in terms of the sulfur content, then depositing 0.05 ~ 10 mass% of palladium on a zirconium hydroxide carrier by impregnating a palladium compound, calcining/stabilizing it at a temperature of 550 ~ 800°C, subsequently mixing alumina or silica-alumina so that it occupies 1 ~ 30 mass% of catalyst and molding the mixture in the shape of catalyst and then calcining/stabilizing the catalyst at a temperature of 550 ~ 800°C.

[Claim 4] A method of preparation which is a method for preparing the hydrodesulfurization catalyst according to Claim 1 or 2 and comprises depositing 0.05 ~ 10 mass% of palladium on a zirconium hydroxide carrier by impregnating a palladium compound, next treating it with a treating agent for giving a sulfate radical thereto, depositing 1 ~ 3 mass% of sulfate radical in terms of the sulfur content, calcining/stabilizing it at a temperature of 550 ~ 800°C, subsequently mixing alumina or silica-alumina so that it occupies 1 ~ 30 mass% of catalyst and

molding the mixture in the shape of catalyst and then calcining/stabilizing the catalyst at a temperature of 550 ~ 800°C.

[Claim 5] A preparing method which is a method for preparing the hydrodesulfurization catalyst according to Claim 1 or 2 and comprises depositing 0.05 ~ 10 mass% of palladium on a zirconium hydroxide carrier by impregnating a palladium compound, then mixing alumina or silica-alumina so that it occupies 1 ~ 30 mass% of catalyst and molding the mixture and subsequently treating a zirconium hydroxide carrier with a treating agent for giving a sulfate radical thereto, depositing 1 ~ 3 mass of sulfate radical in terms of the sulfur content, and calcining/stabilizing the catalyst at a temperature of 550 ~ 800°C.

[Claim 6] A preparing method which is a method for preparing the hydrodesulfurization catalyst according to Claim 1 or 2 and comprises treating a zirconium hydroxide carrier with a treating agent for giving a sulfate radical thereto, depositing 1 ~ 3 mass% of sulfate radical in terms of the sulfur content, then mixing alumina or silica-alumina so that it occupies 1 ~ 30 mass% of catalyst and molding the mixture, depositing 0.05 ~ 10 mass% of palladium by impregnating a palladium compound, and calcining/stabilizing it at a temperature of 550 ~ 800°C.

[Claim 7] A preparing method which is a method for preparing the hydrosulfurization catalyst according to Claim 1 or 2 and comprises treating a zirconium hydroxide carrier with a treating agent for giving a sulfate radical thereto, depositing 1 ~ 3 mass% of sulfate radical in terms of the sulfur content and depositing 0.05 ~ 10 mass% of palladium by impregnating a palladium compound, calcining/stabilizing it at a temperature of 550 ~ 800°C, then mixing alumina or silica-alumina so that it occupies 1 ~ 30 mass% of catalyst and molding the mixture and calcining/stabilizing it at a temperature of 550 ~ 800°C.

[Claim 8] A preparing method which is a method for preparing the hydrosulfurization catalyst according to Claim 1 or 2 and comprises mixing alumina or silica-alumina so that it occupies 1 ~ 30 mass% of catalyst and molding the mixture, then treating a zirconium hydroxide carrier with a treating agent for giving a sulfate radical thereto, depositing 1 ~ 3 mass% of sulfate radical in terms of the sulfur content, subsequently depositing 0.05 ~ 10 mass% of palladium by impregnating a palladium compound, calcining/stabilizing it at a temperature of 550 ~ 800°C.

[Claim 9] A preparing method which is a method for preparing the hydrosulfurization catalyst according to Claim 2 and comprises carrying out a step for depositing 0.05 ~ 10 mass%

of one, two or more selected from platinum, rhenium, ruthenium, cobalt and molybdenum on the basis of catalyst simultaneously with any steps prior to calcination and stabilization or among the steps in the method of preparation according to any of Claims 3 to 8.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to a catalyst which is used in hydrodesulfurization treatment of hydrocarbon oils and reduces the sulfur content of a light hydrocarbon oils containing organic sulfur compounds. In more detail, the present invention relates to a catalyst which has no need of a preplimentary sulfurization treatment which was necessary as a pretreatment of reaction with a conventional desulfurization catalyst in a hydrodesulfurization using a solid ultrastrong acid catalyst and gives a high activity for reducing the sulfur content in hydrocarbon oils at a comparatively low reaction temperature. The present invention also relates to preparing methods of such a catalyst.

[0002]

[Prior Art] Various hydrocarbon fractions obtained by distillation and decomposition of crude oil contain more or less

sulfur compounds, when these oils are used as fuels, sulfur oxides due to the oils are emitted and pollute the air. Recently, further lowering of sulfur has also been required from problems of environmental pollution for gasoline and light oils used as fuels of automobiles and airplanes.

[0003] Now, light hydrocarbon oils, such as light naphtha which has been used as gasoline base, usually contain about 400

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~ 700 ppm of organic sulfur, therefore the sulfur content is reduced to 70 ~ 150 ppm by Merox treatment or the sulfur content is reduced by treatment with Co-Mo series, Ni-Mo series hydrodesulfurization catalysts, etc. The sulfur content of intermediate fractions such as light oil, etc. is about 1 ~ 2%, therefore the sulfur content is reduced to 500 ppm or less by treatment with hydrodesulfurization catalysts like the desulfurization of naphtha, but it is required that the sulfur content be further reduced in the future by enhancement of environmental control.

[0004] With hydrodesulfurization catalysts which have been used so far, however, the more sufficiently the sulfur content is reduced according to the future control, the higher the desulfurization activity will not be exhibited, thus appearance of a desulfurization catalyst with more excellent activity than



conventional catalysts has been desired. In addition, with the Co-Mo series, Ni-Mo series hydrodesulfurization catalysts, a preliminary sulfurization is needed as a pretreatment of the hydrodesulfurization, steps not only are troublesome but also unfavorable in economy.

[0005] As one solution measure on this problem, an acid catalyst based on zirconium sulfate has been disclosed more recently (Japan Kokai H11-197510). This catalyst is a solid acid catalyst containing zirconium sulfate and a hydrogenation transition metal such as platinum and has a specific surface area of  $135 \text{ m}^2/\text{g}$  or above, a pore volume of  $0.16 \text{ mL/g}$  and a mean pore diameter of  $2 \text{ nm}$  or above.

[0006] The inventors also studied on a hydrodesulfurization catalyst combining a platinum family metal with zirconium sulfate (wrong word "zirconia sulfate" in original document, translator), discovered and already proposed a catalyst having both high desulfurization activity of light hydrocarbons and high isomerization performance (Japan Appl. 11-324242). The catalyst is characterized in that it is made by containing  $1 \sim 3 \text{ mass\%}$  of sulfate radical in zirconium oxide or hydroxide in terms of the sulfur content, depositing  $0.05 \sim 10 \text{ mass\%}$  of palladium (or also  $0.05 \sim 10 \text{ mass\%}$  of platinum) and then

calcining/stabilizing at a temperature of 550 ~ 800°C, and the specific surface area is 50 ~ 150 m<sup>2</sup>/g or above.

[0007] The inventors who further advanced the study discovered that a specific solid ultrastrong acid catalyst had excellent desulfurization activity and can also effectively reduce the sulfur content in hydrocarbon oils at a comparatively low reaction temperature even if a preliminary sulfurization was not carried out as a pretreatment of the desulfurization.

[0008]

[Problem to Be Solved by the Invention] The purpose of present invention is to provide a hydrodesulfurization catalyst which is a catalyst used in hydrodesulfurization for hydrocarbon oils, does not require a preliminary sulfurization being a treatment step before use, has high hydrodesulfurization activity and is effective at a comparatively low temperature by best use of the above new knowledge obtained by the inventors.

[0009]

[Means for Solving the Problem] The invented hydrodesulfurization catalyst for hydrocarbon oils which is characterized in that the catalyst is made by depositing 1 ~ 30 mass% of alumina or silica-alumina, 1 ~ 3 mass% of sulfate radical in terms of the sulfur content and 0.05 ~ 10 mass% of palladium on a carrier consisting of zirconium oxide or hydroxide, the total

pore volume is 0.1 mL/g or above and the proportion of pores of 1.4 ~ 2.1 nm in pore diameter therein is 30 ~ 70%.

[0010] 0.05 ~ 10 mass% of one, two or more selected from platinum, rhenium, ruthenium, cobalt and molybdenum can also be further deposited in this catalyst.

[0011] The hydrodesulfurization method for hydrocarbon oils using the invented catalyst comprises carrying out the hydrodesulfurization by bringing a hydrocarbon fraction containing organic sulfur component and hydrogen into contact with this catalyst under conditions of hydrogen partial pressure 1 ~ 15 MPa, temperature 50 ~ 350°C, liquid-space velocity 0.1 ~ 15 hr<sup>-1</sup>, and hydrogen/oil ratio 50 ~ 1,500 NL/L.

[0012]

[Embodiments of the Invention] A carrier for invented catalyst is zirconium oxide or hydroxide as described above. Forms  $\text{Zr}(\text{OH})_4$ ,  $\text{Zr}(\text{OH})_2$ ,  $\text{Zr}(\text{OH})_3$ , etc. are given as zirconium hydroxide, all of them may be used, but a form expressed by a hydrate of zirconium oxide  $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$  (however,  $0 \leq x \leq 2$ ) is commonly suitable.

[0013] It is preferable from a viewpoint of catalyst strength that alumina or silica-alumina is contained in the carrier consisting of zirconium oxide or hydroxide. The content is 1 ~ 30 mass%, preferably 3 ~ 25 mass% on the basis of

catalyst. If the content is less than 1 mass%, the catalyst strength is low and unsuitable as an industrial catalyst; on the other hand, if the content is more than 30 mass%, the catalyst strength is enough, but the desulfurization catalyst activity reduces.

[0014] The invented solid ultrastrong acid catalyst preferably has SCS (i.e., Side Crush Strength, a value representing the mechanical strength of catalyst) of 0.5 kg/mm or above. If SCS is less than 0.5 kg/mm, it is feared that the catalyst has a low strength, breaks and disintegrates when the catalyst is packed into a reactor. If catalyst grains disintegrate, it is feared that the differential pressure in equipment increases and the operation of hydrogenation treatment cannot be continued.

[0015] As palladium compounds used to deposit palladium on the carrier, chlorometallic acid salts, chlorides, sulfates, nitrates, acetates, tetramine-palladium complex, etc. can be given. Preferable are chlorides, sulfates and nitrates.

[0016] The content of palladium is 0.05 ~ 10 mass%, preferably 0.1 ~ 5 mass% on the basis of catalyst. If the deposited amount of palladium is less than 0.05 mass%, the desulfurization activity is not manifested; if it is more than

10 mass%, the dispersibility of palladium being an active metal reduces and the activity reduces instead.

[0017] As treating agents for giving sulfate radical ( $\text{SO}_4$ ) to

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a carrier, sulfuric acid, ammonium sulfate, or hydrogen sulfide, sulfur dioxide, etc. are given. Sulfuric acid and ammonium sulfate are easy to use. The amount of sulfate radical is taken as 1 ~ 3 mass%, preferably 1.5 ~ 2 mass% in terms of sulfur (S) content. If the amount of sulfate radical in terms of sulfur is less than 1 mass%, the acidity of catalyst, i.e., the solid ultrastrong acidity is weak and the activity as desulfurization catalyst is insufficient. If the amount is more than 3 mass% and becomes considerable, the sulfate radical excessively covers the surface of zirconium carrier and piles up at the surface and collapses the activity sites, therefore the activity reduces instead.

[0018] Determination of the sulfur content in catalyst is carried out by burning a sample in an oxygen stream, oxidizing S contained in the sample into  $\text{SO}_2$ , removing moisture and dust and then detecting S with an infrared detector, e.g., a solid-state detector. By this analytic method, the sulfur content in sample can be obtained within a concentration range of 0.001 ~ 99.99%.

[0019] It is required that the invented hydrodesulfurization catalyst have the total pore volume of 0.1 mL/g or above, preferably within a range of 0.1 ~ 0.25 mL/g after it is calcined and stabilized at a prescribed temperature, and a proportion occupied therein by pores having a pore diameter of 1.4 ~ 2.1 nm be 30 ~ 70%. If the total pore volume does not reach 0.1 mL/g, a high catalyst activity is not obtained. If the volume of pores having a pore diameter within the above range is less than 30% of the total pore volume, the desulfurization activity sites decrease and sufficient desulfurization activity is not obtained. If it is more than 70%, the desulfurization activity can be fully obtained, but the catalyst strength reduces. A preferable range is 35 ~ 65%.

[0020] The above pore diameter and pore volume can be measured and calculated by nitrogen adsorption method using a common measuring apparatus for surface area and pore volume.

[0021] In a preferable mode of the invented catalyst, as described above, the desulfurization activity can be further raised by adding one, two or more metals selected from platinum, ruthenium, rhenium, cobalt and molybdenum in a palladium-containing catalyst. The amount of these metals is 0.05 ~ 10 mass%, preferably 0.05 ~ 5 mass%. If the amount is less than 0.05 mass%, an effect of improving the desulfurization activity

is not found; if it is more than 10 mass%, the dispersibility of active metals reduces, and there is a possibility that the desulfurization activity rather reduces.

[0022] As physical properties after the invented solid ultrastrong acid catalyst is calcined and stabilized, the abundance ratio of monoclinic crystal structure and tetragonal crystal structure in the crystal structure of zirconium oxide ( $\text{ZrO}_2$ ) as carrier is preferably within a range of monoclinic crystal/tetragonal crystal = 20/80 ~ 0/100, more preferably within a range of 10/90 ~ 0/100. This is because the tetragonal crystal has high activity as a catalyst carrier, if the ratio of monoclinic crystal structure is high, the catalyst activity reduces therewith. The abundance ratio of monoclinic crystal structure and tetragonal crystal structure in zirconium oxide can be obtained by measuring the X-ray diffraction peaks of catalyst and then calculating it with the integral intensity ratio of X-ray diffraction peaks of a peak  $2\theta = 28.2$  (main peak of monoclinic crystal structure) based on  $\text{CuK } \alpha$  line and a peak  $2\theta = 30.2$  (main peak of tetragonal crystal structure).

[0023] After the invented solid ultrastrong acid catalyst is calcined and stabilized, the specific surface area is preferably within a range of 50 ~ 200  $\text{m}^2/\text{g}$ , and more preferably within a range of 50 ~ 150  $\text{m}^2/\text{g}$ . If the specific surface area is

less than  $50 \text{ m}^2/\text{g}$ , the dispersibility of deposited metals is low and the activity sites for hydrodesulfurization also decreases. For a catalyst with a low specific surface area, the crystal structure of zirconium oxide is undesirable from this viewpoint because the ratio of monoclinic crystal and tetragonal crystal becomes greater than 20/80. If the specific surface area is low, it also becomes difficult to secure the content of sulfate radical in catalyst to be 1 mass% or above in terms of sulfur content, thus the solid ultrastrong acidity does not manifest. On the other hand, if the specific surface area is more than  $200 \text{ m}^2/\text{g}$ , the crystallization of zirconium oxide does not proceed, the ratio of tetragonal crystal structure of zirconium oxide therein is at a low level, therefore the hydrodesulfurization activity is stopped to a low value and thus is undesirable. A value measured by BET method is used as the above specific surface area.

[0024] There are no special limitations in the method for preparing the invented catalyst, and methods and order for giving a sulfate radical and depositing palladium are also arbitrary, if suitable specific examples are given, any of the following methods may be used.

(1) A process wherein sulfate radical is first contained in a zirconium hydroxide carrier, dried, then palladium metal is



impregnated and deposited, dried and calcined, successively an inorganic oxide such as alumina sol or the like is mixed, then molded, dried and calcined

(2) A process wherein an active metal is first impregnated and deposited on a zirconium hydroxide carrier, dried, sulfate radical is contained, dried and calcined, next an inorganic oxide such as alumina sol or the like is mixed, then molded, dried and calcined

(3) A process wherein palladium metal is first impregnated and deposited on a zirconium hydroxide carrier, an inorganic oxide such as alumina sol or the like is mixed, molded, dried and calcined, then sulfate radical is contained, dried and calcined

(4) A process wherein sulfate radical is first contained, molded, dried and calcined, an inorganic oxide such as alumina sol or the like is mixed therewith, then palladium metal is impregnated, dried and calcined

(5) A process wherein sulfate radical and palladium metal are simultaneously deposited on a zirconium hydroxide carrier, dried and calcined, then an inorganic oxide such as alumina sol or the like is mixed, molded, dried and calcined

(6) A process wherein an inorganic oxide such as alumina sol or the like is mixed at the beginning, molded and dried,

then sulfate radical is contained and dried again, next palladium metal is impregnated and deposited, then dried and calcined.

[0025] When platinum, ruthenium, rhenium, cobalt or molybdenum being the second metal component in addition to palladium is used, its deposition can be carried out by the same method as the deposition of palladium, these metals may be introduced in an step before the calcination and stabilization. Of course, they may also be introduced simultaneously with palladium.

[0026] A preparing method of the invented catalyst will be specifically described with the above preparing process of above (1) below.

[0027] First, a sulfate radical treatment is conducted for a material of carrier consisting of zirconium hydroxide or oxide. This sulfate radical treatment is carried out by adding a sulfate dissolved in water to zirconium hydroxide or oxide, then filtered and dried. As treating agents for giving a sulfate radical, 0.1 ~ 5 N sulfuric acid, 0.1 ~ 10 M ammonium sulfate, hydrogen sulfide and sulfur dioxide, etc. are given, but preferable ones are sulfuric acid and ammonium sulfate as described above.

[0028] An impregnation method and a blending method are given as methods for sulfate radical treatment. The impregnation method is a method wherein 1 ~ 10 equivalent of a treating agent being a liquid is impregnated into a catalyst carrier, then filtered and dried. For example, drying is conducted by heating at 110°C for 1 ~ 24 hr. The blending method is a method wherein a treating agent in solid state is blended with a carrier and contained as a sulfate radical treating agent. It does not matter to use any of blending machines commonly used in preparation of catalysts as blending means. A liquid can also be added as a viscosity modifier. As added liquids, water, solvents such as ethanol, isopropanol, acetone, methyl ethyl ketone, diethyl ketone, methyl isobutyl ketone, etc. are given. In this case, the addition order of the sulfate radical treating agent and solvent is not specially limited, the blending temperature and time are not limited so long as physical properties expected for the invented catalyst are provided under these conditions.

[0029] Next, palladium metal is deposited on the sulfate radical-containing carrier. Palladium can be contained by dipping a carrier in an aqueous solution of its chlorometallic acid salts, chloride, sulfate, nitrate, acetate or tetramine-palladium complex, etc., lifting up the carrier and then drying. The drying is conducted at a temperature of 110°C for 1 ~ 24 hr.

As another method, a technique wherein the metal and sulfate radical are simultaneously deposited by mixing and blending chloride, sulfate or nitrate, etc. of palladium metal during blending with the above sulfate radical treating agents.

[0030] A calcination/stabilization treatment is applied to the carrier on which sulfate radical and palladium metal are deposited. The calcination/stabilization treatment is a treatment conducted by heating at a temperature range of 550 ~ 800°C, preferably 600 ~ 750°C under an oxidative atmosphere for 0.5 ~ 10 hr. If the calcination temperature is lower than 550°C, the ratio of zirconium hydroxide contained in a zirconium compound increases and the ratio of tetragonal crystal occupied in zirconium oxide decreases, therefore properties of a solid acid do not manifest and the hydrosulfurization activity of catalyst is low. By contrast, if the carrier is heat-treated at a high temperature of above 800°C, the ratio of zirconium hydroxide decreases, but the ratio of monoclinic crystal occupied in zirconium oxide increases and the hydrosulfurization activity reduces. Not only that much, the sulfate radical is also eliminated from the catalyst, the sulfur content in catalyst becomes less than 1 mass% and the solid acid intensity reduces, Moreover, sintering of deposited metal such

as palladium also occurs, thus activity sites of hydrodesulfurization decrease.

[0031] A reason why the calcination/stabilization treatment of catalyst is conducted under an oxidative atmosphere is because the combined state of a metal such as palladium, etc. or a metallic compound and a sulfate radical changes if it is conducted under a reductive atmosphere or the catalyst activity reduces due to a decrease of sulfate radicals attributed to reductive decomposition.

[0032] It does not matter whether the above calcination/stabilization treatment is conducted before or after a metal such as palladium or the like is deposited. When the treatment is conducted before a metal is deposited, the calcination/stabilization is carried out within a range of 550 ~ 800°C, more preferably 600 ~ 750°C, which is a temperature for obtaining zirconium oxide with a tetragonal crystal structure as crystalline state, and the calcination temperature is preferably within a range of 0.5 ~ 10 hr. When the calcination/stabilization is carried out, a metal such as palladium or the like is deposited and subsequently a stabilization treatment for calcining it at a temperature of 300 ~ 700°C is conducted, the catalyst can also be activated.

[0033] The palladium-deposited and sulfate radical-contained zirconia obtained in this manner is then mixed with alumina or silica-alumina as a binder and molded into a catalyst. Although various forms of alumina can be used as raw material of alumina, aluminas in the form of alumina hydroxide, boehmite or pseudo-boehmite are preferable. Silica sol is suitable as raw material of silica. The preparation of catalyst comprises mixing the palladium-deposited and sulfate radical-contained zirconia and, e.g., alumina sol, molding, drying and then conducting the calcination/stabilization treatment. The invented catalyst can also be obtained by mixing the palladium-deposited and sulfate radical-contained zirconia and boehmite powder, adding water and other media to impart the fluidity, then conducting molding treatment, drying and then calcination.

[0034] When alumina is used as a binder, as described in the above catalyst preparing processes (1) ~ (6), the catalyst may also be prepared by a procedure of mixing zirconium hydroxide and alumina, then conducting treatments for giving sulfate radical and palladium metal, etc. and subsequently molding, drying and calcination.

[0035] The shape of catalyst is not specially limited, and various shapes which can be usually taken by this kind of

catalyst, for example, cylinder, quaterfoil type, etc. obtained by tablet molding or extrusion molding can be adopted.

[0036] The preparation of catalyst for depositing platinum, ruthenium, rhenium, cobalt and molybdenum in addition to palladium, which is a preferable mode of the present invention, can be carried out by the same technique as the method for depositing palladium. Namely, an aqueous solution of chlorometallic acid salts, chlorides, sulfates, nitrates, acetates, tetramine complexes of these metals is impregnated into a carrier simultaneously with palladium or separately and

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then dried. A method wherein metals are deposited and sulfate radical is imparted simultaneously by blending chlorides, sulfates, nitrates, etc. when blending with the sulfate radical treating agent can also be adopted.

[0037] As stock oils for carrying out hydrodesulfurization with the invented solid ultrastrong acid catalyst, hydrocarbon oils containing organic sulfur, such as light naphtha, heavy naphtha, kerosene, light oil, etc. are suitable. A particularly suitable stock oil is a light naphtha with ASTM distillation temperature of 25 ~ 130°C, preferably 25 ~ 110°C. Light naphtha with the content of organic sulfur of about 700 mass ppm,

preferably about 10 ~ 500 mass ppm can be effectively desulfurized.

[0038] Conditions of desulfurization for hydrocarbon oils using the invented catalyst are as follows.

Reaction temperature: 50 ~ 350°C, preferably 100 ~ 280°C

Hydrogen partial pressure: 1.0 ~ 15 MPa, preferably 1.4 ~ 5 MPa

LHSV: 0.1 ~ 15 hr<sup>-1</sup>, preferably 1.0 ~ 8 hr<sup>-1</sup>,

Hydrogen/oil ratio: 50 ~ 1,500 NL/L, preferably 100 ~ 1,000 NL/L

[0039] If the reaction temperature is lower than 50°C, the catalyst activity is too low, on the other hand, if it is above 350°C, the decomposition of hydrocarbon oil proceeds and the yield of production oil reduces. As seen in actual examples described later, an advantage of this catalyst consists in that a high desulfurization activity is exhibited at a comparatively low temperature of 100 ~ 200°C. Other conditions, i.e., hydrogen partial pressure, liquid-space velocity and hydrogen/oil ratio are nearly the same as conditions for the desulfurization of hydrocarbon oil carried out before.

[0040] For the invented solid ultrastrong acid catalyst, a preliminary sulfurization which has been carried out as a pretreatment of reaction for the conventional desulfurization



catalyst is unnecessary, instead, it is preferable to apply a reduction treatment for reduction of deposited metallic compounds to metals and activation of strong acid sites. This reduction treatment is preferably carried out by drying the catalyst at a temperature of 100 ~ 500°C for 1 ~ 24 hr under an atmosphere of hydrogen gas or inactive gas and then reducing it at a temperature of 100 ~ 400°C under an atmosphere of hydrogen gas.

[0041]

[Actual Examples] The present invention will be described in detail by giving Actual Examples 1 ~ 17 (preparation of catalysts A ~ J, N and P ~ T) and Comparative Examples 1 ~ 5 (preparation of catalysts K\*, L\* and O\* and commercial catalysts U\* and V\*) and showing examples of hydrodesulfurization using these catalysts). However, the present invention is not limited by these examples. (a sign \* indicates that it is a comparative example.)

[0042] [Actual Example 1] Catalyst A

(1) Preparation of  $\text{Zr}(\text{OH})_4$

1,000 g of a commercial zirconium oxychloride  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  was dissolved in 4 L of distilled water, a 25% ammonia water  $\text{NH}_3\text{aq}$  was dropped thereto while stirring, and zirconium hydroxide  $\text{Zr}(\text{OH})_4$  was precipitated. An aqueous solution was prepared so

that its pH became 9.0, and the precipitated zirconium hydroxide was filtered and separated. After the filtration, it was well washed with distilled water and dried at 110°C for a whole day and night to give 490 g of zirconium hydroxide.

(2) Preparation of  $\text{SO}_4/\text{Zr}(\text{OH})_4$

400 g of zirconium hydroxide prepared from zirconium oxychloride in the above manner was put into 4,000 g of 1 N sulfuric acid and stirred for 30 min. After stirring, it was filtered, and the solid was dried at 110°C for a whole day and night to give 452 g of a sulfate radical-containing zirconium hydroxide  $\text{SO}_4/\text{Zr}(\text{OH})_4$ .

(3) Preparation of  $\text{Pd}/\text{SO}_4/\text{ZrO}_2$

190 g of zirconium hydroxide with a sulfate radical was put into a solution dissolving 1.8 g of palladium chloride  $\text{PdCl}_2$  in hydrochloric acid, and the Pd salt was impregnated. Subsequently, it was dried at 110°C for a whole day and night, and 135 g of a raw material of Pd-deposited and sulfate radical-containing zirconia catalyst ( $\text{Pd}/\text{SO}_4/\text{ZrO}_2$ ) was obtained by calcining it at 600°C for 3 hr with a Muffle furnace.

(4) Preparation of  $\text{Pd}/\text{SO}_4/\text{ZrO}_2\text{-Al}_2\text{O}_3$

100 g of raw material of catalyst obtained by the above operation and 60 g of alumina sol were fully mixed, molded into cylinders of 1.6 mm in diameter through an extrusion molding

machine, and dried at 110°C for a whole day and night. 109 g of a catalyst A was obtained by calcining and stabilizing it at 600°C again.

[0043] [Actual Example 2] Catalyst B

151 g of a catalyst B was obtained by carrying out impregnation, drying, molding and calcination under same conditions as Actual Example 1 except that 1.9 g of palladium sulfate was used in place of palladium chloride and 200 g of zirconium hydroxide containing sulfate radical was used in Actual Example 1.

[0044] [Actual Example 3] Catalyst C

175 g of a catalyst C was obtained by carrying out impregnation, drying, molding and calcination under same conditions as Actual Example 1 except that 1.8 g of palladium nitrate was used in place of palladium chloride and 166 g of sulfate radical-containing zirconium hydroxide was used in Actual Example 1.

[0045] [Actual Example 4] Catalyst D

149 g of a catalyst D was obtained by carrying out impregnation, drying, molding and calcination under same conditions as Actual Example 1 except that 2.0 g of palladium chloride monohydrate was used in place of palladium chloride and

139 g of sulfate radical-containing zirconium hydroxide was used in Actual Example 1.

[0046] [Actual Example 5] Catalyst E

A catalyst E was obtained by carrying out impregnation and drying under same conditions as Actual Example 1 except that 30 g of aluminum sol was used in Actual Example 1, preparing a pellet of 3 mm in diameter and then calcining it.

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[0047] [Actual Example 6] Catalyst F

A catalyst F was obtained by carrying out impregnation and drying, molding and calcination under same conditions as Actual Example 1 except that 90 g of aluminum sol was used in Actual Example 1.

[0048] [Actual Example 7] Catalyst G

A catalyst G was obtained by carrying out impregnation and drying, molding and calcination under same conditions as Actual Example 1 except that 120 g of aluminum sol was used in Actual Example 1.

[0049] [Actual Example 8] Catalyst H

A catalyst H was obtained by carrying out impregnation and drying, molding and calcination under same conditions as Actual Example 1 except that 54 g of aluminum sol was used and 6 g of silica sol was supplemented in Actual Example 1.

[0050] [Actual Example 9] Catalyst I

A catalyst I was obtained by carrying out impregnation and drying, molding and calcination under same conditions as Actual Example 1 except that 36 g of aluminum sol was used and 24 g of silica sol was supplemented in Actual Example 1.

[0051] [Actual Example 10] Catalyst J

A catalyst J was obtained by carrying out impregnation and drying, molding and calcination under same conditions as Actual Example 1 except that 108 g of aluminum sol was used and 12 g of silica sol was supplemented in Actual Example 1.

[0052] [Comparative Example 1] Catalyst K\*

A catalyst K\* was obtained by carrying out impregnation and drying, molding and calcination under same conditions as Actual Example 1 except that alumina was not mixed and a tablet molding machine was used in Actual Example 1.

[0053] [Comparative Example 2] Catalyst L\*

A catalyst L\* was obtained by carrying out impregnation and drying, molding and calcination under same conditions as Actual Example 1 except that 1.9 g of platinum chloride was used in place of palladium chloride and 200 g of sulfate radical-containing zirconium hydroxide was used in Actual Example 1.

[0054] Preparation conditions and physical properties of the above catalysts A ~ L are collected and shown in Table 1.

Table 1

Preparation conditions and physical properties of catalysts (1)

	Catalyst A	Catalyst B	Catalyst C	Catalyst D
Deposited substance	PdCl <sub>2</sub>	PdSO <sub>4</sub>	Pd(NO <sub>3</sub> ) <sub>2</sub>	Pd(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub>
Calcination condition	600°C×3hr	600°C×3hr	600°C×3hr	600°C×3hr
Specific surface area (m <sup>2</sup> /g)	134	133	138.4	132.4
Sulfur content (mass%)	1.74	1.53	1.81	1.56
Assay value of metallic elements (mass%)				
Pd	0.51	0.45	0.58	0.70
Crystal structure ratio of ZrO <sub>2</sub>				
Monoclinic crystal/tetragonal crystal	3.5/96.5	3.7/96.3	4.1/95.9	4.3/95.7
Inorganic metal oxide	alumina	alumina	alumina	alumina
Content (mass%)	10	10	10	10
Shape of catalyst	1.6 mmφ cyl.	1.6 mmφ cyl.	1.6 mmφ cyl.	1.6 mmφ cyl.
SCS (xg/mm)	0.6	0.5	0.6	0.6
Pore volume (mL/g)	0.154	0.151	0.157	0.153
Proportion occupied by pore volume of 1.4 ~ 2.1 nm (%)	45.7	44.6	44.7	46.1

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Table 1

## Preparation conditions and physical properties of catalysts (2)

	Catalyst E	Catalyst F	Catalyst G	Catalyst H
Deposited substance	PdCl <sub>2</sub>	PdCl <sub>2</sub>	PdCl <sub>2</sub>	PdCl <sub>2</sub>
Calcination condition	600°C×3hr	600°C×3hr	600°C×3hr	600°C×3hr
Specific surface area (m <sup>2</sup> /g)	116.1	146.1	161.0	141.7
Sulfur content (mass%)	1.83	1.64	1.54	1.63
Assay value of metallic elements (mass%)				
Pd	0.53	0.48	0.44	0.49
Crystal structure ratio of ZrO <sub>2</sub>				
Monoclinic crystal/tetragonal crystal	3.5/96.5	3.7/96.3	4.1/95.9	4.3/95.7
Inorganic metal oxide	alumina	alumina	alumina	silica- alumina (10:90)
Content (mass%)	5	15	20	10
Shape of catalyst	3 mmφ pellet	1.6 mmφ cyl.	1.6 mmφ cyl.	1.6 mmφ cyl.
SCS (kg/mm)	0.8	0.6	0.8	0.7
Pore volume (mL/g)	0.130	0.178	0.202	0.170
Proportion occupied by pore volume of 1.4 ~ 2.1 nm (%)	60.3	36.2	31.0	35.4

[0056]

Table 1

## Preparation conditions and physical properties of catalysts (3)

	Catalyst I	Catalyst J	Catalyst K*	Catalyst L*
Deposited substance	PdCl <sub>2</sub>	PdCl <sub>2</sub>	PdCl <sub>2</sub>	H <sub>2</sub> PdCl <sub>4</sub>
Calcination condition	600°C×3hr	600°C×3hr	600°C×3hr	600°C×3hr
Specific surface area (m <sup>2</sup> /g)	119.1	137.2	101.1	132.4
Sulfur content (mass%)	1.75	1.50	1.92	1.90
Assay value of metallic elements (mass%)				
Pd	0.52	0.46	0.55	-
Pt	-	-	-	0.60
Crystal structure ratio of ZrO <sub>2</sub>				
Monoclinic crystal/tetragonal crystal	3.5/96.5	3.7/96.3	3.5/96.5	4.3/95.7
Inorganic metal oxide	silica- alumina (40:60)	silica- alumina (10:90)	-	alumina
Content (mass%)	10	20	0	10
Shape of catalyst	3 mmφ pellet	1.6 mmφ cyl.	3 mmφ cyl.	1.6 mmφ cyl.
SCS (kg/mm)	0.9	0.8	< 0.1	0.6
Pore volume (mL/g)	0.134	0.160	0.107	0.158
Proportion occupied by pore volume of 1.4 ~ 2.1 nm (%)	57.5	40.1	76.8	45.9

A high-precision fully automatic gas adsorption apparatus [BELSORP 28] made by Nippon Bell Corp. was used for measurement of specific surface area. The sulfur content was determined by an SC-132 sulfur analyzer made by LECO Co.

[0057] [Actual Example 11] Catalyst M

1.5 g of palladium chloride  $\text{PdCl}_2$  was put into 20 g of water, 30 cc of concentrated hydrochloric acid was dropped and dissolved by applying an ultrasonic wave for 10 min to give a first solution. Separately, 1.6 g of chloroplatinic acid hexahydrate  $\text{H}_2\text{PdCl}_6 \cdot 6\text{H}_2\text{O}$  was dissolved in 10 g of water to give a second solution. 172.9 g of the sulfate radical-containing zirconium hydroxide prepared in Actual Example 1 was put into a mixed solution of the first and second solutions, the Pd salt and Pt salt were impregnated and deposited. Thereafter, Pd/Pt/ $\text{SO}_4/\text{ZrO}_2\text{-Al}_2\text{O}_3$  was obtained by carrying out mixing alumina sol, molding drying, and calcination similarly as step (4) of Actual Example 1.

[0058] [Actual Example 12] Catalyst N

1.5 g of palladium chloride  $\text{PdCl}_2$  was put into 20 g of water, 30 cc of concentrated hydrochloric acid was dropped and dissolved by applying an ultrasonic wave for 10 min to give a first solution. Separately, 1.6 g of chloroplatinic acid hexahydrate  $\text{H}_2\text{PdCl}_6 \cdot 6\text{H}_2\text{O}$  was dissolved in 10 g of water to give a second solution. 174.2 g of the sulfate radical-containing



zirconium hydroxide was put into a mixed solution of these solutions, the Pd salt and Pt salt were impregnated and deposited. Thereafter, Pd/Pt/SO<sub>4</sub>/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> was obtained by carrying out mixing alumina sol, molding drying, and calcination similarly as step (4) of Actual Example 1.

[0059] [Comparative Example 3] Catalyst O\*

2.2 g of palladium chloride PdCl<sub>2</sub> was put into 20 g of water, 30 cc of concentrated hydrochloric acid was dropped and dissolved by applying an ultrasonic wave for 10 min to give a first solution. Separately, 2.5 g of chloroplatinic acid hexahydrate H<sub>2</sub>PdCl<sub>6</sub>·6H<sub>2</sub>O was dissolved in 10 g of water to give a second solution. 170 g of the above sulfate radical-containing zirconium hydroxide was put into a mixed solution of these solutions, the Pd salt and Pt salt were impregnated and deposited. Thereafter, Pd/Pt-deposited and sulfate radical-containing zirconia Pd/Pt/SO<sub>4</sub>/ZrO<sub>2</sub> was obtained by carrying out drying and calcination similarly as Actual Example 1. Pd/Pt/SO<sub>4</sub>/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> was obtained by mixing 210 g of alumina sol with 100 g obtained Pd/Pt-deposited and sulfate radical-containing zirconia, extrusion molding, drying at 110°C for a whole day and night and then calcining at 600°C for 3 hr.

[0060] [Actual Example 13] Catalyst P

1.5 g of palladium chloride  $\text{PdCl}_2$  was put into 20 g of water, 30 cc of concentrated hydrochloric acid was dropped and dissolved by applying an ultrasonic wave for 10 min to give a first solution. Separately, 1.2 g of rhenium oxide  $\text{Re}_2\text{O}_7$  was dissolved in 10 g of water to give a second solution. 170 g of the above sulfate radical-containing zirconium hydroxide was put into a mixed solution of these solutions, the Pd salt and Re salt were impregnated and deposited. Thereafter,  $\text{Pd/Re/SO}_4/\text{ZrO}_2\text{-Al}_2\text{O}_3$  was obtained by mixing alumina and carrying out molding, drying and calcination similarly as step (4) of Actual Example 1.

[0061] [Actual Example 14] Catalyst Q

1.5 g of palladium chloride  $\text{PdCl}_2$  was put into 20 g of water, 30 cc of concentrated hydrochloric acid was dropped and dissolved by applying an ultrasonic wave for 10 min to give a first solution. Separately, 1.9 g of rhenium chloride  $\text{RuCl}_3$  was

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dissolved in 10 g of water to give a second solution. 171.1 g of the above sulfate radical-containing zirconium hydroxide was put into a mixed solution of these solutions, the Pd salt and Pt salt were impregnated and deposited. Thereafter, Pd/Pt-deposited and sulfate radical-containing zirconia  $\text{Pd/Ru/SO}_4/\text{ZrO}_2\text{-Al}_2\text{O}_3$  was

obtained by carrying out molding, drying and calcination similarly as step (4) of Actual Example 1.

[0062] [Actual Example 15] Catalyst R

1.5 g of palladium chloride  $\text{PdCl}_2$  was put into 20 g of water, 30 cc of concentrated hydrochloric acid was dropped and dissolved by applying an ultrasonic wave for 10 min to give a first solution. Separately, 2.2 g of rhenium chloride  $\text{RuCl}_3$  was dissolved in 10 g of water to give a second solution. 169.5 g of the above sulfate radical-containing zirconium hydroxide was put into a mixed solution of these solutions, the Pd salt and Pt salt were impregnated and deposited. Thereafter,  $\text{Pd/Ru/SO}_4/\text{ZrO}_2\text{-Al}_2\text{O}_3$  was obtained by carrying out molding, drying and calcination similarly as step (4) of Actual Example 1.

[0063] [Actual Example 16] Catalyst S

1.5 g of palladium chloride  $\text{PdCl}_2$  was put into 20 g of water, 30 cc of concentrated hydrochloric acid was dropped and dissolved by applying an ultrasonic wave for 10 min to give a first solution. Separately, 4.5 g of cobalt nitrate hexahydrate  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in 10 g of water to prepare a second solution. 170.9 g of the above sulfate radical-containing zirconium hydroxide was put into a mixed solution of these solutions, the Pd salt and Pt salt were impregnated and deposited. Thereafter,  $\text{Pd/Co/SO}_4/\text{ZrO}_2\text{-Al}_2\text{O}_3$  was obtained by

carrying out molding, drying and calcination similarly as step (4) of Actual Example 1.

[0064] [Actual Example 17] Catalyst T

1.5 g of palladium chloride  $\text{PdCl}_2$  was put into 20 g of water, 30 cc of concentrated hydrochloric acid was dropped and dissolved by applying an ultrasonic wave for 10 min to give a first solution. Separately, 1.7 g of ammonium p-molybdate  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  was dissolved in 10 g of water to give a second solution. 170.4 g of the above sulfate radical-containing zirconium hydroxide was put into a mixed solution of these solutions, the Pd salt and Pt salt were impregnated and deposited. Thereafter,  $\text{Pd/Mo/SO}_4/\text{ZrO}_2\text{-Al}_2\text{O}_3$  was obtained by carrying out molding, drying and calcination similarly as step (4) of Actual Example 1.

[0065] [Comparative Example 4] A commercial Co-Mo desulfurization catalyst U\* with alumina as a carrier was used.

[0066] [Comparative Example 5] A commercial Co-Mo desulfurization catalyst V\* with alumina as a carrier was used.

[0067] Preparation conditions and physical properties of the catalysts of Actual Examples 11 ~ 17 and Comparative Example 3 are collected and shown in Table 1.

Table 2

## Preparation conditions and physical properties of catalysts (4)

	Catalyst M	Catalyst N	Catalyst O*	Catalyst P
Deposited substance	$\text{PdCl}_2/\text{H}_2\text{PtCl}_6$	$\text{PdCl}_2/\text{H}_2\text{PtCl}_6$	$\text{PdCl}_2/\text{H}_2\text{PtCl}_6$	$\text{PdCl}_2/\text{Re}_2\text{O}_7$
Calcination condition	600°C×3hr	600°C×3hr	600°C×3hr	600°C×3hr
Specific surface area ( $\text{m}^2/\text{g}$ )	149	144.9	191.1	143.5
Sulfur content (mass%)	1.96	1.90	1.64	1.84
Assay value of metallic elements (mass%)				
Pd	0.47	0.98	0.52	0.48
Pt	0.43	0.49	0.49	-
Re	-	-	-	0.48
Crystal structure ratio of $\text{ZrO}_2$				
Monoclinic crystal/tetragonal crystal	4.0/96.0	3.5/96.5	3.5/96.5	3.6/96.4
Inorganic metal oxide	alumina	alumina	alumina	alumina
Content (mass%)	10	10	35	10
Shape of catalyst	1.6 mmφ cyl.	1.6 mmφ cyl.	1.6 mmφ cyl.	1.6 mmφ cyl.
SCS (kg/mm)	0.6	0.6	1.0	0.6
Pore volume (mL/g)	0.156	0.160	0.245	0.153
Proportion occupied by pore volume of 1.4 ~ 2.1 nm (%)	45.5	44.4	22.7	46.7

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[0068]

Table 2

Preparation conditions and physical properties of catalysts (5)

	Catalyst Q	Catalyst R	Catalyst S	Catalyst T
Deposited substance	PdCl <sub>2</sub> /RuCl <sub>3</sub>	PdCl <sub>2</sub> /RuCl <sub>3</sub>	PdCl <sub>2</sub> /Co(NO <sub>3</sub> ) <sub>3</sub>	PdCl <sub>2</sub> / (NH <sub>4</sub> ) MoO <sub>4</sub> O <sub>23</sub>
Calcination condition	600°C×3hr	600°C×3hr	600°C×3hr	600°C×3hr
Specific surface area (m <sup>2</sup> /g)	144	141.5	140.0	144.6
Sulfur content (mass%)	2.11	2.04	1.74	1.64
Assay value of metallic elements (mass%)				
Pd	0.47	0.46	0.49	0.52
Ru	0.49	1.01	-	-
Co	-	-	0.49	-
Mo	-	-	-	0.49
Crystal structure ratio of ZrO <sub>2</sub>				
Monoclinic crystal/tetragonal crystal	5.5/94.5	4.6/95.4	3.6/96.4	3.1/96.9
Inorganic metal oxide	alumina	alumina	alumina	alumina
Content (mass%)	10	10	10	10
Shape of catalyst	1.6 mmφ cyl.	1.6 mmφ cyl.	1.6 mmφ cyl.	1.6 mmφ cyl.
SCS (kg/mm)	0.5	0.6	0.6	0.6
Pore volume (mL/g)	0.155	0.151	0.158	0.154
Proportion occupied by pore volume of 1.4 ~ 2.1 nm (%)	46.6	44.3	47.0	45.5

[0069] [Examples for Catalyst Use] Evaluation method for hydrodesulfurization of hydrocarbon oil

The desulfurization activity of catalysts A ~ J and L ~ T, excluding catalyst K with SCS of less than 0.5 kg/mm, was evaluated by packing a catalyst in a fixed-bed flow-type reactor with a catalyst packing volume of 15 mL, feeding unwashed naphtha as a stock hydrocarbon oil and carrying out hydrodesulfurization under conditions of Table 3. The catalysts were crushed to 16 ~ 28 mesh before the packing. The commercial desulfurization catalysts of Comparative Examples 4 and 5 were

used in the hydrodesulfurization as they were without conducting preliminary sulfurization as a pre-treatment.

[0070]

Table 3  
Conditions for hydrodesulfurization

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Reaction conditions: Reaction temperature: 160°C

Hydrogen partial pressure : 3.0 MPa

Liquid-space velocity: 1 hr

Hydrogen/oil ratio: 300 NL/L

Stock: unwashed naphtha (S content 384 mass  
Ppm)

Behavior of stock oil	Density:	g/cm <sup>3</sup> (15°C)	0.6534
	Distillation behavior	IBP °C	29.5
	5% distillation temperature	°C	39.5
	10% distillation temperature	°C	40.5
	50% distillation temperature	°C	49.0
	70% distillation temperature	°C	54.5
	90% distillation temperature	°C	63.5
	95% distillation temperature	°C	66.5
	EP	°C	98.5
	Sulfur content	mass ppm	384
	Saturated content	vol%	98.53

Unsaturated content	vol%	0.07
Aromatic content	vol%	1.40

[0071] Results of hydrodesulfurization are shown in Table 4 with employed catalysts.

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Table 4  
Results of hydrodesulfurization of light naphtha

Catalyst	Composition	Sulfur Removal Percentage (%)
Catalyst A of Actual Example 1	Pd/SO <sub>4</sub> /ZrO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	97.2
Catalyst B of Actual Example 2	Pd/SO <sub>4</sub> /ZrO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	96.8
Catalyst C of Actual Example 3	Pd/SO <sub>4</sub> /ZrO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	96.5
Catalyst D of Actual Example 4	Pd/SO <sub>4</sub> /ZrO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	96.0
Catalyst E of Actual Example 5	Pd/SO <sub>4</sub> /ZrO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	98.5
Catalyst F of Actual Example 6	Pd/SO <sub>4</sub> /ZrO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	97.0
Catalyst G of Actual Example 7	Pd/SO <sub>4</sub> /ZrO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	95.0
Catalyst H of Actual Example 8	Pd/SO <sub>4</sub> /ZrO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	96.7
Catalyst I of Actual Example 9	Pd/SO <sub>4</sub> /ZrO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>	97.4
Catalyst J of Actual Example 10	Pd/SO <sub>4</sub> /ZrO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>	95.9
Catalyst M of Actual Example 11	Pd/SO <sub>4</sub> /ZrO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>	98.5
Catalyst N of Actual Example 12	Pd/Pt/SO <sub>4</sub> /ZrO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	98.9
Catalyst P of Actual Example 13	Pd/Pt/SO <sub>4</sub> /ZrO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	98.7
Catalyst Q of Actual Example 14	Pd/Re/SO <sub>4</sub> /ZrO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	98.5
Catalyst R of Actual Example 15	Pd/Ru/SO <sub>4</sub> /ZrO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	98.1
Catalyst S of Actual Example 16	Pd/Ru/SO <sub>4</sub> /ZrO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	98.5
Catalyst T of Actual Example 17	Pd/Co/SO <sub>4</sub> /ZrO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	98.8
Catalyst L* of Comparative Example 2	Pd/Mo/SO <sub>4</sub> /ZrO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	33.3
Catalyst O* of Comparative Example 3	Pt/SO <sub>4</sub> /ZrO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	63.7
Catalyst U* of Comparative Example 4	Pd/Pt/SO <sub>4</sub> /ZrO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	50.8
Catalyst V* of Comparative Example 5	Co-Mo	46.0
	Co-Mo	

[0072] From the above data, it is known that a high sulfur removal percentage of over 95% could be obtained in all of Actual Examples 1 ~ 17 using the catalysts according to the



present invention. In Comparative Example 2 (catalyst L\*) wherein palladium being an important constituent of the invented catalyst is not deposited and Comparative Example 3 (Catalyst O\*, 22.7%) wherein the proportion of pore volume having pore diameter of 1.4 ~ 2.1 nm is less than 30 ~ 70% has the sulfur removal percentage of 63.7% and is also lower than those of Actual Examples.

[0073] In Comparative Examples 4 & 5 using commercial Co-Mo desulfurization catalysts, the sulfur removal percentages of the both are as low as about 50% as compared with the actual examples where the hydrodesulfurization was carried out without preliminary sulfurization as a pretreatment of reaction.

[0074]

[Effects of the Invention] The solid acid catalyst having specific physical properties according to the present invention can reduce the sulfur contained in hydrocarbon oils with good efficiency. In the prior hydrodesulfurization catalyst, preliminary sulfurization was necessary as a pre-treatment of reaction, by contrast, the invented catalyst has no need of pre-treatment and displays a high desulfurization even if it is directly used. The invented catalyst exhibits a high desulfurization activity even at such a comparatively low temperature as 160°C given in the above actual examples. Thus,

when the invented catalyst is applied to the hydrodesulfurization of hydrocarbon oils, it enables to favorably carry out the hydrodesulfurization in the industry.